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## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification 5 :</b>  A01N 37/06, 65/00	<b>A1</b>	<b>(11) International Publication Number:</b> WO 91/18508  <b>(43) International Publication Date:</b> 12 December 1991 (12.12.91)
<b>(21) International Application Number:</b> PCT/EP91/00972 <b>(22) International Filing Date:</b> 27 May 1991 (27.05.91)  <b>(30) Priority data:</b> 20441 A/90                      28 May 1990 (28.05.90)                      IT 21206 A/90                      3 August 1990 (03.08.90)                      IT  <b>(71) Applicant (for all designated States except US):</b> SOSTRA S.R.L. [IT/IT]; Via Carroccio, 8, I-20123 Milano (IT).  <b>(72) Inventor; and</b> <b>(75) Inventor/Applicant (for US only) :</b> FORMIGONI, Attilio [IT/IT]; Via Pietro Micca, 11, I-20025 Legnano (IT).  <b>(74) Agents:</b> FAGGIONI, Marco et al.; Fumero Studio Consulenza Brevetti, Via S. Agnese, 12, I-20123 Milano (IT).		<b>(81) Designated States:</b> AT (European patent), AU, BE (European patent), BR, CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, LU (European patent), NL (European patent), SE (European patent), US.  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> COMPOSITION AGAINST OZONE DAMAGES TO CULTIVATIONS AND METHOD FOR ITS APPLICATION  <b>(57) Abstract</b>  Composition to prevent ozone damages to cultivations, based on fatty acids of natural origin, both as such or as their salts or esters, like the triglycerides in oils or fats of vegetable or animal origin, preferably containing a high percentage of unsaturated fatty acids, possibly with the addition of antioxidants, chelating compounds for heavy metals, plant growth regulators, leafage fertilizers with macroelements, oligo-elements and chelated microelements, and possibly with emulsifiers, surfactants and inerts. Method for applying said composition by atomizing the same on the leaves in concentrated form, or diluted in solvents or emulsified in water, during the plants vegetation period, so as to prevent ozone from damaging the cultivations.		

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"COMPOSITION AGAINST OZONE DAMAGES TO CULTIVATIONS AND METHOD FOR ITS APPLICATION"

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#### BACKGROUND OF THE INVENTION

##### 5 Field of the Invention

The damages caused by ozone to field and tree cultivations - even if ozone is present at the height of the cultivation to a very slight extent (for instance, 0.03-0.10 ppm by weight in the atmosphere) - have been widely described since very many years, said damages being  
10 represented either by leafage necrosis, or by reduced flower fertilization and less production of fruits, seeds and leaves, with a considerably reduced productiveness of several cultivations.

Such damages have mostly been noticed in the agricultural regions of the more developed countries as, for example, North America,  
15 Europe, and the industrialized areas of other Continents, and they are generally tied to an increase in the ozone concentration at the height of the cultivation, determined by a simultaneous increase of air pollution originated from different pollutants. Ozone ( $O_3$ ) at the height of the cultivation is in fact formed starting from atmospheric oxygen ( $O_2$ ), as a  
20 result of a photochemical reaction favoured by a bright sun radiation and by the presence of air pollutants, as nitrogen oxides, with the catalytic activity of different hydrocarbons, such pollutants being mostly present in highly industrialized areas. Nevertheless, such air pollutants are not only present where they are originated, but they are also carried away by  
25 the winds through long distances, thereby producing ozone also in agricultural regions which are very far from the polluting sources.

Though considering the more or less intense varietal sensitivity of the different plants, in various cases high damages caused by the presence of ozone have been noticed on several harvests, such as to justify  
30 the search for different means allowing to reduce such damages.

##### Description of the Prior Art

In the last decades, various products have been described allow-

ing to reduce ozone damages to different plants, even if with occasional-  
ly contrasting results (for example: Siegel S.M., Plant Physiol. 37,261  
(1962); Dass H.C. and Weaver G.M., Can. J. Plant Sci. 48,569 (1968);  
Thompson C.R. & G. Katz. Calif. Agric., 24 (9) 12-13 (1970); Manning W.J.  
5 and Vardaro P.M., Phytopathology 63, 1415 (1973); Hager F.M., German Pat.  
Appl. 2.238.053 (1973); Tomlinson H. and Rich S., Phytopathology 63, 903  
(1973); Moyer J. et Al., Plant Dis. Rep. 58, 41-44 (1974); Takaoka J. et  
Al., Japan Pat. Appl. 75/40763 (1975); Gilbert M.D. et Al., Hort. Sci.  
10,228-231 (1975); Walker J.T. and J. Melin, Plant Dis. Rep. 62,400  
10 (1978); Hofgstra G. et Al., Plant Dis. Rep. 62,350 (1978); Okii M. et  
Al., U.S. Pat. 4,231,789 (1980); Rubin B. et Al., Bull. Environ. Contam.  
Toxicol. 25, 623 (1980); Beckerson D.W. and D.P. Ormond, Hort. Sci.  
21,1070 (1986)).

In particular, to reduce ozone damages to plants, use has been  
15 made at times of antioxidants (as ascorbic acid, propylgallate, alpha-to-  
copherol, diphenylamine); of plant growth regulators (as abscissic acid,  
cytoquinines); of thiocarbamic, benzimidazolic, triazolic or oxathiinic  
fungicides; of insecticide synergists (as piperonyl butoxide); or even of  
various amines, or other compounds (as glutathione) and - more frequently  
20 - the compound coded EDU (N-(2-oxo-1-imidazolydiny)ethyl-N'-phenylurea)  
and derivatives (U.S. Patents 3,859,301, 3,973,946 and 4,055,412; Carna-  
han J.E. et Al., Phytopathology 68,1225 (1978)), the EDU being adopted as  
standard also recently in an international research project (O'Sullivan  
D.A. Chem. & Drug Eng. News 67,7 (1989)).

25 It should nevertheless be pointed out that, after several deca-  
des of different searches in this field, none of the products developed  
so far is currently used for commercial purposes, and even the EDU com-  
pound is no longer commercially produced, both for reasons of costs -  
which are too high against economically unacceptable results - and for  
30 toxicological problems, deriving from the risk of pollution of the cul-  
tivations treated with chemical compounds which are potentially harmful  
if present as residues in food.

SUMMARY OF THE INVENTION

The object of the present invention is to therefore make up for the shortages existing in the phytosanitary field, in respect of the prevention of damages caused to cultivations by tropospheric ozone, by supplying a composition of reduced cost and not toxic for the plants, as well as for the animals and for mankind, which is useful to reduce the  
aforecited ozone damages.

Another object of the present invention is to supply a method and a dosage to apply said composition, allowing to obtain the best results in reducing ozone damages.

According to the invention, said objects are reached by means of a composition based on fatty acids of natural origin, preferably unsaturated, or their salts and esters, as in particular the triglycerides contained in oils and fats of vegetable or animal origin. Said composition is preferably applied with a method according to which it is distributed on the plants, before any ozone damages are caused thereto, by being atomized thereon in an amount of between 0.1 and 100 litres per hectare of fatty acids or of oils or fats.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS OF THE INVENTION

It is known that the double bond between carbon atoms of olefinic compounds reacts with ozone to form intermediates of different composition, generically defined as ozonides, with subsequent decomposition thereof and formation of different compounds, giving rise to the process defined as ozonolysis, usually employed in organic chemistry to study the molecular structures of unsaturated organic compounds, either synthetic or natural.

However, in order to easily obtain such ozonolysis reaction, it is necessary to operate with laboratory methods such as to allow the reaction to take place in a quantitative way and within acceptable times.

It is necessary, for instance, to usually operate with the unsaturated compound diluted in a solvent which is inert for ozone (as chloroform, carbon tetrachloride, glacial acetic acid, low boiling saturated

fractions of petroleum, and so on), through which is caused to flow an air stream enriched with a high ozone concentration.

To allow the subsequent rapid decomposition of the formed ozonides, it is useful to treat them with reducing agents in order to obtain aldehydes and/or ketones, or to oxidize them so as to obtain acid derivatives.

It is also known that natural oils and fats containing unsaturated fatty acids, if exposed to air for a certain time, slowly undergo oxidation due to the action of atmospheric oxygen, more frequently with the formation of small quantities of hydroperoxides on the alpha carbon close to the double bond, with subsequent cracking of the double bond and formation of different compounds (as aldehydes and/or ketones).

In natural conditions, ozonolysis does not take place rapidly in a quantitative way, owing to the very low ozone concentration normally existing at the tropospheric level (for example, 0.01-0.07 ppm).

It is known, in fact, that if unsaturated fatty acids of natural origin, or their salts and esters, are caused to react in the presence of air containing very low ozone concentrations - equivalent to those existing in natural conditions - the reaction kinetics is such as to require very long reaction times (for example, several years) in order to react the ozone present in such a low concentration and thereby reduce the ozone level, in natural conditions, below the plant damaging threshold.

From the above it ensues that the expert of the art, though being acquainted with the reactivity of ozone with olefinic compounds, under controlled laboratory conditions and in the presence of high ozone concentrations, was not led to consider important - from the quantitative point of view and from that of the reaction speed - the reactivity of unsaturated fatty acids of natural origin, or of their salts and esters, in a natural environment, that is, in presence of air with very low ozone concentrations. Furthermore, the chemical reactions through which ozone damages the plants after penetrating into the leaves through the stomata, are widely known: in fact, ozone reacts inside the leaves with the double

bonds of the unsaturated organic compounds present in the membranes and in other cell components, forming at first ozonides from which various peroxidized free radicals are then released damaging different enzymatic reactions, with disturbance of the cell walls permeability and with distortion of the photosynthesis process and of the proteic metabolism of the plants (Hewitt C.N. et Al., Chemistry and Industry, Aug. 1990, 478-481).

It is also known that the volatile olefinic compounds produced by plants and present, for example, in the air of forest regions, react - even if not quantitatively - with tropospheric ozone, producing a large number of free radicals with subsequent formation of hydroperoxides (Martinez R.I. et Al., J. Am. Chem. Soc. 103, 3807-3820 (1981); Hellpoinster E. and Gab S., Nature 337, 631-634 (1989)).

Such free radicals and hydroperoxides which form in the air of agricultural regions, helped also by the favourable action of humidity, could lead to an increase of the endogenous damages caused to plants by ozone, once they had penetrated into the leaves through breathing of the plant (Becker K.H. et Al., Nature 346, 256-258 (1990)).

To thus reduce ozone damages to cultivations, on the basis of the data published in scientific literature, the expert of the art would have been led to consider the use of natural unsaturated fatty acids or their salts and esters as fully useless from the practical point of view, since it involves very long reaction kinetics in natural conditions; on the other hand, he would have been faced with the doubt that such olefinic compounds, on reacting - though to a minimum extent - with ozone, could have caused in natural conditions the formation of further peroxidized free radicals, particularly harmful for the plants. thereby increasing the damages caused by ozone to cultivations.

Viceversa, the inventor of the present invention was able to discover during his searches that, contrary to all expectations based on known scientific knowledge, if unsaturated fatty acids of natural origin or their salts and esters - like the triglycerides contained in oils and

fats of vegetable and animal origin - are distributed on the cultivations in a suitable way, instead of increasing the damages caused to plants by ozone. they allow to obtain the unexpected result of reducing said damages on the cultivations which have undergone said treatment.

5           On the basis of present scientific knowledge, it has however not been possible, up-to-date, to give a full theoretical explanation to the actual mechanism which determines this fully unexpected result. Factors that are still unknown could in fact be involved, as an unexpected mechanism of enhancement of the reactivity of natural unsaturated fatty acids  
10 with tropospheric ozone at leafage level, following the starting - in said particular environment - of possibly catalyzed self-enhancing chain reactions, which give rise to fully unexpected quantitative results.

          This invention is of considerable importance not only because it makes use of compositions which are generally economic, but also because  
15 such compositions - based on natural fatty acids or their salts and esters, as oils or fats of vegetable or animal origin - are not phytotoxic for the plants in the required doses of use, they apply no polluting substances on the cultivations thus treated, and they are highly biodegradable, without disturbing the biological balance and the natural environment.  
20

          There are a good number of fatty acids of natural origin, which can be usefully employed in a composition against ozone damages to cultivations, but they are all essentially derived from natural oils and fats, both vegetable and animal.

25           Usually, vegetable or animal oils and fats contain mixtures of triglycerides based on fatty acids of different kind, both saturated and unsaturated, which are mostly difficult to separate even with very complicated industrial processes (as hydrolysis at high temperature and high pressure, with use of reagents and catalysts. often operating in vapor  
30 streams or with inert gases. or proceeding by fractioned distillation or by chromatographic separation).

          The result is that the natural fatty acids present on the market



are not pure products, but they generally consist mostly of mixtures wherein there is possibly a predominant component.

Such mixtures usually contain either saturated fatty acids (as caproic, caprylic, capric, lauric, myristic, palmitic, stearic, arachic, behenic, lignoceric acid, and the like), or monounsaturated fatty acids (as caproleic, lauroleic, myristoleic, palmitoleic, oleic, ricinoleic, vaccinic, gadoleic, cetoleic, erucic, brassidic, selacoleic acid, and the like), or even poly-unsaturated fatty acids (as linoleic, linolenic, iragonic, oleostearic, tricosanic, arachidonic, eicosapentenoic acid, and the like).

The most active compositions against ozone damages to cultivations are those containing a higher content of unsaturated fatty acids, even if said unsaturated fatty acids are mixed with saturated fatty acids, as for example compositions with a high content of oleic acid, linoleic acid, linolenic acid, erucic acid, and so on.

The fatty acids of the present invention may be salified by alkaline metals (as sodium, potassium), or they may be esterified with lower alcohols (as methyl, ethyl, isopropyl alcohols, and so on), but more commonly such fatty acids are to be found as triglyceride esters in oils or fats of vegetable origin, or also in oils or fats of animal origin.

There are a great number of vegetable oils and fats which can be most commonly used to reduce ozone damages to cultivations, and they usually originate from the milling and pressing of seeds, or of other parts of various so-called oleiferous plants, often followed by extraction with solvents from the obtained pressed seeds, and possibly also by a further process of rectification and purification.

The vegetable oils which can be used in compositions against ozone damages are, for example, the following: linseed, soybean, cotton, sunflower, corn, safflower, grapestone, rapeseed, peanut, sesame, olive, castor-oil, tall-oil, palm, coconut; though other vegetable oils can be used (as wheat, barley and rice germ oils, cucurbitaceae seed, almond, Neouli, Perilla, Oitica, Tung oils, and so on), but at generally higher

costs.

Even if a large number of vegetable oils are suited for this use, those which have proved to be the most interesting in order to reduce ozone damages are the ones with a higher content of unsaturated fatty acids and, in particular, of poly-unsaturated fatty acids, as for example, oils of linseed, soybean, grapestone, safflower, cotton, corn, sesame, sunflower, tall-oil, and so on; though use can also be made of oils with a lower content of poly-unsaturated fatty acids but rich in mono-unsaturated fatty acids, as olive oil, rapeseed oil, peanut oil, castor-oil and so on.

It is of course also possible to use mixtures of such vegetable oils, as oils of different seeds obtained from by-products, and thus of particularly low cost (for example, mixtures of oils of soybean, cotton, sunflower, peanut, rapeseed, palm, and so on).

Likewise, use can also be made of compositions based on oils or fats derived from animals, obtained for instance from terrestrial Mammalia (bovines, swine, equines, sheep and goats, and so on), as for example tallow oil, olein, bovine feet and bone oil, all obtained with different processes (for example, extraction with solvents subsequently eliminated by distillation, heating up followed by cooling or winterization to separate the lower melting components, or other processes).

Equally, use can be made of compositions based on oils of sea animals, like oils of cetaceans (as whales, sperm-whales), or fish oils (as cods, herrings, sardines, sharks, and so on).

In the event of disposing of fatty substances which are not liquid at ambient temperature, their practical use in a composition according to the invention is possible if such fats are dissolved into suitable solvents (as hydrocarbons, alcohols, ketones or glycols, which are not phytotoxic for the cultivations).

According to a particular aspect of the present invention, some special adjuvants are added to the fatty acids of natural origin, or to their salts and esters, or to the aforementioned oils and fats of vegeta-

ble and animal origin diluted into solvents, which adjuvants have proved in different cases to possess a synergic strengthening effect in reducing the ozone damages.

Such adjuvants with a synergic effect can be grouped into the following categories:

- a) Antioxidants, as propyl-, octyl-, lauryl-gallate, and other gallic acid esters; butyl-hydroxy-toluene; butyl-hydroxy-anisole; ethoxyquin; diphenylamine; naphthyl-phenylamine; ascorbic and erythrorbic acid and their salts and esters; tocopherols; mono- or di-ter-butyl-hydroquinone and other hydroquinones; dithiopropionic acid and its salts and esters; 4-hydroxymethyl-2,6-di-ter-butylphenol; nordihydroguaiaic acid; propylethylguaetol; 2,4,5-tri-hydroxybutyrophenone; and other antioxidants well known to the expert of the art. Such antioxidants can also be used in different mixtures: in fact, the reciprocal strengthening effect of their action is known in various cases.
- b) Chelating compounds for heavy metals - which can reduce the action of the antioxidants - as citric and tartaric acid and their salts and esters; phosphoric acids and their salts and esters; organic chelating compounds as EDTA, HEDTA, DPTA, EDDHA, HEP, heptagluconates, or different aminoacids, also in mixtures derived from hydrolysis of animal or vegetable proteins.
- c) Plant growth regulators, as concentrated extracts from seaweeds containing cytoquinines (zeatine, benzyl- and furfuryl-adenine, and so on), gibberellines, auxines, abscissic acid, or other plant growth regulators of natural or synthetic origin.
- d) Fertilizers, containing macro-elements as nitrogen (for example, nitrogenous inorganic and organic fertilizers, as hydrolized animal epithelia or hydrolized vegetable substances, like soybean proteins, seaweeds, yeasts, fungi or bacteria or fermentation residues, all including polypeptides or aminoacids, as well as other natural substances); or else containing phosphorous (for example, different phosphates), or even potassium (as potassium salts), or containing oligo-elements (as

magnesium, calcium and sulphur) and/or microelements (as boron, molybdenum, iron, manganese, zinc, copper, cobalt, and so on), the heavy metals being preferably present as chelates.

To improve the use of the composition according to the invention  
5 - for instance, with water emulsified compositions - it may eventually be helpful to further add surfactants and/or emulsifiers: for example, mono- and diglycerides of fatty acids and their esters: ethoxylated and/or propoxylated alcohols, alkylphenols, amines, fatty acids, oils and fats; esters of fatty acids, of glycerol and of glycols; lecithin and derivatives;  
10 ves; phosphate and sulphate esters; sorbitan-derivatives; saccharose esters and derivatives; sulphates and sulphonates of oils, of fatty acids, of aromatic and aliphatic derivatives; succinates and their sulphoderivatives; various polyoxyethylene and polyoxypropylene copolymers, and so on (see list of such commercial surfactants and emulsifiers on the publication: McCutcheon's-Detergents & Emulsifiers, Glen Rock, N.J., USA).  
15

The expert of the art shall use said emulsifiers on the basis of the optimal hydrophilic-lipophilic balance that one wishes to obtain for the compositions after their water emulsion, by making use of the most suitable products and/or their mixtures in the optimal quantity, in order  
20 to obtain water stable emulsions, without the forming of persistent foam, eventually also adding further anti-foam agents, as for instance silicone compounds. Also inerts could be added to the composition, as for example different solvents and co-solvents (like alcohols, hydrocarbons, polar solvents, and so on), as well as organic liquids like glycols or even  
25 water (in the event of oil-in-water and water-in-oil emulsions of the "mayonnaise" type), possibly also adding thickening and suspending agents, as alginates or xanthane gum and even bentones.

A composition according to the present invention could thus for example be composed as follows:

30 Fatty acids or their salts and esters (as oils or fats of vegetable or animal origin)

1-100%

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	Antioxidants	0-20%
	Chelating compounds	0-10%
	Plant growth regulators	0-20%
	Surfactants and emulsifiers	0-30%
5	Fertilizers	0-50%
	Inerts (as solvents, suspending and diluting agents)	0-99%

Another object of the present invention is to use a special method for applying said composition - based on fatty acids of natural origin or their salts and esters, as the triglycerides present in oils and fats of vegetable or animal origin - which allows to obtain the best results in reducing ozone damages to cultivations.

The previously described composition according to the invention, based on fatty acids of natural origin or their salts and esters, should be atomized on the cultivations having to be protected from ozone damages in the right periods, that is, before any such damages occur and when the plants are most sensitive thereto, which means before, during and after blossom time, so as to protect flower fertilization, or during and after the leaf growth period, in which ozone penetrates through the stomata causing various damages.

Said technique of preventive defence thus requires the possible repeated use of the composition according to the invention, for instance at intervals of 7-14 or more days, with the object of keeping protected the growing vegetation and of preventing any possible degradation of the composition throughout time, after it has been distributed on the cultivations.

The composition can be applied with suitable equipment (as spray pumps and/or atomizers, operating on ground or also on air means), which distributes on the plants high volumes of liquids (for instance, 500-5000 l/ha), medium volumes (for instance 100-500 l/ha), low volumes (for instance 20-100 l/ha). or even very low volumes of liquids (for instance

1-20 l/ha).

The composition based on fatty acids or their salts and esters, or on vegetable or animal oils or fats, can either be highly concentrated (up to using the fatty acids or the oils as such), or more diluted, by adding various adjuvants and inerts as previously described, and by possible subsequent water emulsion before being atomized on the plants.

In the event of using fatty acids or vegetable or animal oils as such, or in highly concentrated form, it will be necessary to operate with equipment (for instance pneumatic, with rotary nozzles, or the like) apt to atomize fairly reduced quantities of relatively viscous liquids per surface unit, adopting the low or very low volume spraying technique.

Said technique is also very suitable for application by air means (for instance, aircrafts or helicopters).

In the event of using instead a more diluted composition, containing additives, emulsifiers and different adjuvants, use can be made of more common equipment apt to spray on the plants water emulsions of fatty acids or their salts and esters, or of vegetable or animal oils or fats diluted in water, taking care to cover the cultivations as far as possible with finely atomized mixtures, adopting the previously defined atomization technique with low, medium or high volumes of liquids.

It is anyhow particularly important for the compositions to be atomized and/or sprayed in such a way as to cover the sides of the leaves containing the stomata openings, through which ozone penetrates into the leaves.

The doses of use of the composition according to the invention can vary within fairly wide limits, according to the growth of the field or tree cultivations having to be protected, to their lower or higher varietal sensitivity, to the lower or higher levels of ozone present in the air, and thus according to whether the damages which may be caused will be more or less serious, which damages should anyhow be avoided by always using the composition by way of prevention, that is, before any ozone damages occur.

The useful doses of the composition according to the invention will be such as to distribute quantities of fatty acids or their salts and esters, or of vegetable or animal oils and fats, included between 0.1 and 100 litres per hectare: for field cultivations, such quantities may  
5 vary from 0.1 to 50 litres per hectare, with preferential doses of 0.3 to 20 litres per hectare; while for tree cultivations, the quantity having to be distributed may vary from 0.2 to 100 litres per hectare, with preferential doses of 0.6 to 40 litres per hectare.

The composition according to the invention can be distributed on  
10 the cultivations, in different cases, also mixed with chemical products for crop protection (for instance, fungicides, insecticides, acaricides, selective herbicides, and the like), and this can give rise to positive phenomena of mutual interaction.

There are a great number of cultivations which are sensitive to  
15 damages caused by ozone. Among the agricultural ones there are, for example, tobacco, soybean, cotton, sweet-potato, peanuts, white potato, sunflower, rape, flax, safflower, castor bean, sugar beet or forage beet, lucern and clover, forage peas, or cereals as wheat, barley, rice, and minor cereals like rye, oats and triticale, as well as corn and sorghum.  
20 Among the horticultural ones, those more likely to be affected are the Cucurbitaceae (as water-melons, melons, marrows), the Solanaceae (like tomatoes, peppers, aubergines), the leguminous plants (as beans, French beans, broad beans, peas), the cruciferous plants (as cabbage, cauliflower, turnips), the Chenopodiaceae (as spinach, beet-root), the Umbelliferae (as fennel, carrot), the Compositae (as salads of various types  
25 and artichokes), and other horticultural cultivations. Also several floricultural and ornamental plants are sensitive to ozone damages, as for instance, carnations, roses, gerberae, and others. The fruit cultivations which can be protected include vines, Pomaceae (as apples and pears),  
30 Drupaceae (as peaches, plums, cherries, apricots), kiwi, citrus fruits, the berry fruits (as strawberries, black-currant, raspberries, bilberries, and the like), and also the hop.

In various cases and in particular regions, also tropical plants need to be protected. as banana, coffee, tea, sugar-cane, caoutchouc, jute, and the like.

Even ornamental and forest trees are often quite sensitive to ozone damages as, for example, coniferous trees and various broad-leaved trees (as the poplar). In this respect, one should remember the serious problem of the death of forests in the industrialized countries, caused by the presence of ozone, by the concomitant phenomenon of acid rains, by recurrent years of drought, and by different interacting factors.

The examples which follow are meant to illustrate the invention more clearly, without however limiting its possible applications.

#### FORMULATION EXAMPLES

##### Example 1

Highly concentrated compositions of fatty acids, liquid at ambient temperature, or of oils of vegetable or animal origin for use with very low and low volumes of liquid (as 1-100 l/ha) were prepared, using compounds as such, both refined and raw, or else mixing therewith small quantities of adjuvants and/or diluents, apt to facilitate their distribution by atomization with suitable equipment and to improve their effectiveness, as in the following compositions (weight percentages):

Composition N.	1	2	3	4	5	6	7	8
Liquid fatty acids or vegetable or animal oils	90	95	97	98	99	99.7	99	95
Propylene glycol	10							
Isobutyl alcohol		5						2
Sorbitan monolaurate			3					
Ethoxylated castor-oil with 3 moles of ethylene oxide				2				
Polyethoxylated nonylphenol with 9 moles of E.O.					1			





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	Animal epithelium hydrolized with 14% N acids				30		
	Urea 46% N					15	
5	Urea 70% - 30% monopotassium phosphate					50	
	Isobutyl alcohol	6	4				4
	Bentone		1				
	Water				20	45	10

Example 3

- 10 Compositions based on water emulsifiable vegetable oils were prepared by mixing with various emulsifiers and adjuvants as in the following compositions (weight percentages):

Composition N.	18	19	20	21	22	23	24	25
Vegetable oils	90	70	89	77	50	68	40	1
15 Sorbitan monolaurate	4	3	4	5	5	4	4	1
Polyethoxylated castor-oil with 3 moles of E.O.	5	7	5	5	7	5	5	1
Polyethoxylated nonylphenol with 9 moles of E.O.	1	20		1	3	2	1	1
20 Diphenylamine			2					
Propylgallate				3				
Butyl-hydroxy-toluene					20			
Mono-ethyl-citrate				3	10			
25 Dried extracts from Ascophyl- lum seaweeds hydrolized with alkali						20		
Animal epithelium hydroli- zed with 14% N acids							30	

17

	Urea 70% - 30% monopotassium phosphate			50
	Isobutyl alcohol	6	5	
	Bentone		1	
5	Water		20	46

Example 4

Compositions based on liquid fatty acids or vegetable or animal oils, in the form of thicker "mayonnaise" type emulsions or as thinner emulsions, were prepared with suitable equipment by emulsifying the oils with various emulsifiers in the presence of water, according to the following compositions (weight percentages):

Composition N.	26	27	28	29
Vegetable or animal oils	50	60	26	60
Glyceryl-mono-isostearate	3	5		
15 Polyethoxylated glyceryl-mono-isostearate with 20 moles of E.O.	3	5		
Sorbitan mono-oleate			2	6
Polyethoxylated sorbitan mono-oleate with 20 moles of E.O.			2	6
20 Water	44	30	70	28

APPLICATION EXAMPLESExample 5

A sealed cell, containing ozone produced by a special ozonizer, was formed into part of an air-conditioned green-house with automatic regulation of the temperature, humidity and light (by Osram Flora type fluorescent lamps, mixed with mercury-vapor lamps).

The ozone level in the cell was checked with an automatic ozone analyzer Model DASIBI 1018. and said level was maintained so as to repro-

duce the conditions normally present in an open field. in regions with a high ozone formation at the height of the cultivation (for instance, 0.03-0.05 ppm in the morning, 0.05-0.08 ppm in the afternoon, according to the increase in sun radiation).

5 To be noted, moreover, that the introduction of ozone into the cell was started gradually at sunrise and was stopped after sunset, so as to reproduce - also through the time of exposure at the various ozone levels - what happens in nature.

The temperature within the cell was kept - with night and day  
10 cycles - at 20-25°C, and the relative air humidity was kept at 50-70%.

Plants likely to be affected by ozone damages, as tobacco (Virginia Bright variety), or French beans (Pros Gitana variety), or even water-melon (Toro variety), were cultivated in pots of 15 cm diameter, into a normally fertilized and irrigated agricultural soil, and preserved  
15 in the green-house in an ozoneless environment.

When some leaves had grown on the plants, the same were treated with the compositions according to the invention, using special equipment allowing to evenly distribute said compositions on the plants by atomization, after having possibly diluted them into sufficient water, usually  
20 50 ml of liquid mixture for 4 pots and per square meter of surface.

Each composition was in fact sprayed on 4 pots, so as to dispose of statistical repetitions of the experiment, and 8 pots of each plant were not treated but left as untreated witnesses.

After having been preventively treated with the compositions according to the invention, the plants in their pots were introduced into  
25 the ozone cell and kept therein for 7 days.

Together with the plants treated with compositions against ozone damages, also the untreated witness plants were put into the cell.

After 7 days, the plants were removed from the ozone cell for a  
30 few hours and the treatment against ozone was repeated in order to protect the newly grown leaves; the pots were then reintroduced into the ozone cell, together with the untreated witness plants. for 7 more days.

After 14 days from the first treatment, it was proceeded to reckon on the treated plants the percentage of leaf surface damaged by necrotic spots, adopting the conventional technique and converting said damage into percent of leafage necrosis, always in comparison with the damage found on the untreated witness plants.

A first series of results, obtained with various types of liquid fatty acids or of animal oils used in different concentrations, is reported in Table 1. From the data reported in said Table, it can be noticed how the compositions according to the invention, based on liquid fatty acids, on their potassium salts, on alkyl esters or on animal oils, are apt to substantially reduce the damages of leafage necrosis caused by ozone on the treated plants, as compared to the damages which can be found on the untreated plants.

In particular, it can be observed how linoleic acid, its potassium salt or ethyl ester and the fish oils (richer in poly-unsaturated fatty acids) show a stronger activity than that of oleic acid and of tallow oil, which are in any case quite effective.

TABLE 1

Average percent of necrotic leaf surface caused by ozone on different cultivations treated every 7 days, after 14 days of permanence in the ozone cell.

Compositions as N. 9 based on fatty acids and animal oils	Doses ml/m <sup>2</sup> of fatty acids or of oils	Percent leafage necrosis on plants		
		Tobacco Virginia Bright variety	French bean Pros Gitana variety	Water- melon Toro variety
Oleic acid 97%	0.1	20	15	12
	0.5	12	10	8
Linoleic acid 90%	0.1	10	8	5
	0.5	7	5	4

20

	Linolenic acid 80%	0.1	10	7	5
		0.5	3	2	3
	Potassium oleate 95%	0.1	22	15	10
		0.5	10	9	7
5	Potassium linoleate 90%	0.1	12	7	7
		0.5	6	4	3
	Ethyl oleate 95%	0.1	21	15	10
		0.5	10	8	7
10	Ethyl linoleate 90%	0.1	11	10	5
		0.5	5	3	3
	Refined cod oil	0.1	17	10	7
		0.5	10	8	5
	Winterized herring oil	0.1	15	12	10
		0.5	11	7	5
15	Tallow oil	0.1	28	17	15
		0.5	16	12	10
	Untreated witness		50	40	22

Example 6

20 In the ozone cell, the method was carried out using the technique described in Example 5, on Tobacco plants Virginia Bright variety treated with different compositions according to the invention, always taking as comparison untreated witness plants.

25 The results obtained are reported in Table 2, from which it can be noticed how the compositions N. 12 and N. 11, based both on 90% oleic acid and on tallow oil, with addition of antioxidants (respectively propylgallate, added with mono-isopropyl-citrate acting as chelant for heavy metals, and diphenylamine) have allowed to obtain - with equal doses of fatty acids or of oils and of antioxidants - far better results in reducing the ozone damages, thus evidencing an unexpected phenomenon of synergy, between the fatty acid or the animal oil and the antioxidants, in protecting the plants from ozone.

30 It can be noticed, furthermore, how the compositions according

2/

to the invention have a greater effectiveness in respect of the EDU product currently used as an international standard in experiments against ozone damages.

TABLE 2

5                   Average percent of leafage necrosis caused by ozone on different plants treated every 7 days, after 14 days of permanence in the ozone cell.

10	Compositions used	Doses ml/m <sup>2</sup> of oil or of oleic acid	% Leafage necrosis Tobacco Virginia Bright variety
	N. 9 based on	0.01	31
	90% oleic acid	0.1	15
		1	10
15	N. 9 based on	0.01	30
	tallow oil	0.1	25
		1	20
	N. 12 based on	0.01	15
	90% oleic acid	0.1	8
		1	5
20	N. 12 based on	0.01	22
	tallow oil	0.1	17
		1	12
	N. 11 based on	0.01	12
	90% oleic acid	0.1	2
25		1	3
	N. 11 based on	0.01	18
	tallow oil	0.1	12
		1	10
	Propylgallate +	(see Note 1)	42
30	mono-isopropyl-citrate	"	34
		"	25

22

	Diphenylamine	(see Note 2)	40
	"	"	30
	"	"	23
<hr/>			
5	EDU (as such in $\text{g/m}^2$ )	0.01	40
		0.1	35
	Untreated witness		40

Notes to Table 2:

- 1) = Doses of propylgallate and of mono-isopropyl-citrate equivalent to those contained in composition N. 12, with doses of oleic acid or of tallow oil equal to  $0.01-0.1-1 \text{ ml/m}^2$ .
- 2) = Doses of diphenylamine equivalent to those contained in composition N. 11, with doses of oleic acid or of tallow oil equal to  $0.01-0.1-1 \text{ ml/m}^2$ .

Example 7

In the ozone cell, the method was carried out using the technique described in Example 5, on Tobacco Virginia Bright variety, on French beans Pros Gitana variety, and on Water-melons Toro variety, treated with different compositions according to the invention, always taking as comparison untreated witness plants.

The results obtained with various types of vegetable oils used in different concentrations are reported in Table 3. From the data reported in said Table, it can be noticed how the compositions according to the invention, based on various types of vegetable oils, substantially reduce the damages of leafage necrosis caused by ozone on the treated plants, as compared to the damages which can be found on the untreated plants. In particular, it can be observed how raw soybean oil (containing tocopherols and other natural substances) shows an increased activity as compared to that of refined soybean oil.

TABLE 3

Average percent of necrotic leaf surface caused by ozone on dif-



ferent plants treated every 7 days, after 14 days of permanence in the ozone cell.

5	Compositions as N. 18 based on vegetable oils from the plants mentioned below	Percent leafage necrosis on plants			
		Doses ml/m <sup>2</sup> of oils	Tobacco Virginia Bright variety	French bean Pros Gitana variety	Water- melon Toro variety
10	Flax	0.1	5	3	3
		0.5	2	1	0
	Soybean (refined)	0.1	7	3	5
		0.5	3	1	1
15	Cotton	0.1	8	5	6
		0.5	5	2	1
	Safflower	0.1	5	2	3
		0.5	4	2	1
20	Grapestone	0.1	5	2	3
		0.5	3	1	1
	Sunflower	0.1	10	7	5
		0.5	8	3	2
25	Corn	0.1	10	5	5
		0.5	7	4	3
	Peanuts	0.1	12	10	7
		0.5	10	8	5
30	Sesame	0.1	8	4	5
		0.5	6	3	2
	Tall-oil	0.1	7	5	6
		0.5	4	2	3
	Castor-bean	0.1	10	9	6
		0.5	8	7	4
	Rape	0.1	15	11	6
		0.5	7	5	5

## 24

	Olive husk	0.1	15	10	5
		0.5	10	7	6
	Soybean (raw)	0.1	1	0	0
		0.5	1	0	0
5	Untreated witness		40	30	20

Example 5

In the ozone cell the method was carried out, using the technique described in Example 5, on Tobacco plants Virginia Bright variety treated with different compositions according to the invention, always taking as comparison untreated witness plants.

The results obtained are reported in Table 4, from which it can be noticed how the compositions N. 21 and N. 20, based both on linseed oil and on soybean oil, with the addition of antioxidants (respectively propylgallate, added with mono-ethyl-citrate acting as chelant for heavy metals, and diphenylamine) have allowed to obtain - with equal doses of vegetable oils and of antioxidants - far better results in reducing the ozone damages, thus evidencing an unexpected phenomenon of synergy, between the vegetable oils and the antioxidants, in protecting the plants from ozone.

It can be noticed, furthermore, how the compositions according to the invention have a greater effectiveness in respect of the EDU product currently used as an international standard in experiments against ozone damages.

TABLE 4

Average percent of leafage necrosis caused by ozone on different plants treated every 7 days, after 14 days of permanence in the ozone cell.

Compositions used	Doses ml/m <sup>2</sup> of oils	% Leafage necrosis Tobacco Virginia Bright variety
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## 25

	N. 18 based on	0.01	18
	linseed oil	0.1	10
		1	8
5	N. 18 based on	0.01	20
	soybean oil	0.1	13
		1	10
	N. 21 based on	0.01	11
	linseed oil	0.1	3
		1	0
10	N. 21 based on	0.01	13
	soybean oil	0.1	4
		1	0
	N. 20 based on	0.01	12
	linseed oil	0.1	2
15		1	0
	N. 20 based on	0.01	13
	soybean oil	0.1	5
		1	0
20	Propylgallate +	(see Note 1)	70
	mono-ethyl-citrate	"	50
		"	35
	Diphenylamine	(see Note 2)	70
		"	30
		"	20
25	EDU (as such	0.01	50
	in g/m <sup>2</sup> )	0.1	30
	Untreated witness		70

## Notes to Table 4:

- 30 1) = Doses of propylgallate and of mono-ethyl-citrate equivalent to those contained in composition N. 21, with doses of oils equal to 0.01-0.1-1 ml/m<sup>2</sup>.
- 2) = Doses of diphenylamine equivalent to those contained in composition N. 20, with doses of oils equal to 0.01-0.1-1 ml/m<sup>2</sup>.

Example 9

French beans of the Pros Gitana variety and Water-melons of the Toro variety were sown on two different plots of land of a field with slimy-sandy soil, duly fertilized and irrigated, and the plants were divided into lots of 20 m<sup>2</sup> (4x5 m) for the French beans, and of 40 m<sup>2</sup> (8x5 m) for the Water-melons, so that each composition according to the invention could be applied separately on each lot, having at the side of each treated lot an equal surface of untreated witness plants.

The same type of experiment was repeated 4 times for each cultivation and for each type of treatment, with statistical distribution, applying the compositions during the following periods:

- before blossom time
- during blossom time
- after blossom time

and subsequently repeating the treatment every 12 days up to harvesting time.

When each treatment was carried out, the ozone level present in the air was detected with the portable DRAEGER analyzer, noticing on an average, half-way through the afternoon, 0.03-0.05 ppm of ozone in the first vegetation periods (May/June) and 0.05-0.07 ppm of ozone in the periods which followed (July/August).

Table 5 shows the compositions tested and the results obtained. The results reported in Table 5 reveal how the compositions according to the invention, based on 90% oleic acid or on tallow oil, allow to obtain also on field - in presence of harmful ozone levels - significant reductions in the damages to leaves.

From Table 5 it can also be seen that the most productive results can be obtained using the compositions N. 11 (oleic acid or tallow oil with addition of diphenylamine as antioxidant), or N. 14 (oleic acid or tallow oil with addition of dried extracts from Ascophyllum type seaweeds hydrolized with alkali, which are rich in natural plant growth regulators), or even N. 15 (oleic acid or tallow oil with addition of

animal epithelium hydrolized with acids, containing 14% of organic nitrogen). These results clearly prove that such compositions - mixed with an antioxidant, or with seaweed extracts containing natural plant growth regulators, or even with a fertilizer based on organic nitrogen obtained from hydrolysis of animal epithelium - give rise to an unexpected synergic strengthening action, with the additional advantages deriving therefrom.

It is in fact remarkable how the use of the antioxidant or of the seaweed extracts or of the hydrolized epithelium, all as such - in doses corresponding to those contained in the compositions according to the invention - is not apt to reduce the percentages of leafage damages; whereas, the different mixtures allow to considerably increase the effectiveness of the compositions based only on oleic acid or on tallow oil (Composition N. 9).

TABLE 5

Average percent of leafage necrosis and unitary production at harvesting time on field cultivations, in presence of harmful ozone levels and with various anti-ozone treatments repeated during the vegetation period.

Compositions used	Doses ml/m <sup>2</sup> of oleic acid or tallow oil	Percent leafage necrosis on plants	
		French bean Pros Gitana variety	Water-melon Toro variety
N. 9 based on	0.1	20	21
25 90% oleic acid	1	15	12
N. 9 based on	0.1	25	28
tallow oil	1	18	20
N. 11 based on	0.1	12	15
90% oleic acid	1	5	7
30 N. 11 based on	0.1	15	20
tallow oil	1	5	12

28

	N. 14 based on	0.1	18	17
	90% oleic acid	1	12	5
	N. 14 based on	0.1	20	22
	tallow oil	1	13	11
5	N. 15 based on	0.1	12	15
	90% oleic acid	1	7	10
	N. 15 based on	0.1	18	20
	tallow oil	1	12	0
	Diphenylamine	(see Note 1)	30	36
	"	"	20	30
10	Dried extracts from	(see Note 2)	32	35
	hydrolized seaweeds	"	30	36
	Hydrolized	(see Note 3)	31	39
	animal epithelium	"	28	30
	Untreated witness		30	35
15	Notes to Table 5:			
	1) = Doses of diphenylamine equivalent to those contained in composition			
	N. 11, with doses of oleic acid or tallow oil equal to $0.1-1 \text{ ml/m}^2$ .			
	2) = Doses of dried extracts from seaweeds hydrolized with alkali, equi-			
	valent to those contained in composition N. 14, with doses of oleic			
20	acid or tallow oil equal to $0.1-1 \text{ ml/m}^2$ .			
	3) = Doses of animal epithelium hydrolized with acids, equivalent to			
	those contained in composition N. 15, with doses of oleic acid or			
	tallow oil equal to $0.1-1 \text{ ml/m}^2$ .			

Example 10

25 French beans of the Pros Gitana variety and Water-melons of the Toro variety were sown on two different plots of land of a field with slimy-sandy soil, duly fertilized and irrigated, operating with the same method reported in Example 9. Table 6 reports the compositions tested and the results obtained.

30 The results reported in Table 6 show how the compositions accor-

ding to the invention, based on vegetable oils. allow to obtain also on field - in presence of harmful ozone levels - significant reductions in the damages to leaves and considerable production increases.

From Table 6 it can also be seen that the most productive results can be obtained using the compositions N. 20 (linseed oil or soybean oil with addition of diphenylamine as antioxidant), or N. 23 (linseed oil or soybean oil with addition of dried extracts from *Ascophyllum* type seaweeds hydrolized with alkali, which are rich in natural plant growth regulators), or even N. 24 (linseed oil or soybean oil with addition of animal epithelium hydrolized with acids, containing 14% of organic nitrogen), or N. 17 (soybean oil with addition of laurylgallate and of urea). These results clearly prove that such compositions - based on vegetable oils mixed with an antioxidant, or with seaweed extracts containing natural plant growth regulators, or even with a fertilizer based on organic nitrogen obtained from hydrolysis of animal epithelium - give rise to an unexpected synergic strengthening action, with the additional advantages deriving therefrom.

It is in fact remarkable how the use of the antioxidant or of the seaweeds extract or of the hydrolized epithelium, all as such - in doses corresponding to those contained in the compositions according to the invention - is not apt to increase production in respect of the untreated witness plants and to reduce the percentages of leafage damage; whereas, the different mixtures have a considerably increased effectiveness in respect of the compositions based only on vegetable oils (Composition N. 18 based on linseed oil or on soybean oil).

TABLE 6

Average percent of leafage necrosis and unitary production at harvesting time on field cultivations, in presence of harmful ozone levels and with various anti-ozone treatments repeated during the plants vegetation period.

	Compositions used	Doses ml/m <sup>2</sup> of oils	French bean Pros Gitana var.		Water-melon Toro variety	
			% leafage necrosis	Produce kg/m <sup>2</sup>	% leafage necrosis	Produce kg/m <sup>2</sup>
5	N. 18 based on linseed oil	0.1	10	0.40	18	4.2
		1	5	0.42	10	5.4
	N. 18 based on soybean oil	0.1	12	0.39	15	4.0
		1	6	0.42	7	5.0
10	N. 20 based on linseed oil	0.1	5	0.51	5	7.5
		1	2	0.64	2	7.9
	N. 20 based on soybean oil	0.1	7	0.49	7	7.2
		1	3	0.54	2	7.8
	N. 23 based on linseed oil	0.1	6	0.50	10	6.9
		1	1	0.69	3	7.9
15	N. 23 based on soybean oil	0.1	7	0.45	12	6.6
		1	2	0.52	5	7.5
	N. 24 based on linseed oil	0.1	7	0.60	10	6.5
		1	3	0.65	1	6.8
20	N. 24 based on soybean oil	0.1	8	0.52	12	6.2
		1	3	0.54	4	6.4
	N. 17 based on soybean oil	0.1	8	0.50	7	7.3
		1	3	0.52	3	7.7
	Diphenylamine	(see Note 1)	33	0.20	42	2.2
		"	30	0.22	46	2.4
25	Dried extracts from hydrolized seaweeds	(see Note 2)	30	0.25	34	2.2
		"	25	0.24	35	2.8
	Hydrolized animal epithelium	(see Note 3)	32	0.20	40	2.0
		"	30	0.22	42	2.5
	Urea 46% N + laurylgallate	(see Note 4)	34	0.20	46	2.2
		"	36	0.23	48	2.3
30	Untreated witness		35	0.21	50	2.3

Notes to Table 6:



with preventive treatments using anti-ozone compositions at emergence, earing and blossom time, carried out with different distribution techniques.

	Compositions used	Doses ml/m <sup>2</sup> of oils	Production in grains at harvesting time (at 13.5% of humidity) kg/100 m <sup>2</sup>
5	Raw linseed oil as such with low volume of liquid	0.5 5	45.3 50.2
10	Raw soybean oil as such with low volume of liquid	0.5 5	42.3 48.5
	Composition N. 4 based on sunflower oil as such with low volume of liquid	0.5 5	41.5 46.5
15	Composition N. 4 based on grapestone oil as such with low volume of liquid	0.5 5	44.5 51.6
	Composition N. 21 based on corn oil in 300 l/ha water	0.5 5	48.6 54.7
20	Composition N. 21 based on rapeseed oil in 300 l/ha water	0.5 5	45.6 50.2
	Composition N. 21 based on oil of different seeds (50% soybean, 30% sunflower, 20% rapeseed) in 300 l/ha water	0.5 5	49.5 55.2
25	Untreated witness		40.2

#### Example 11

In a Clone 314 poplar plantation, aged 15 years, plots of one hectare each were treated twice - at intervals of 30 days, during the period of maximum growth of the leaves - with compositions according to the invention, operating with atomizers using a low or high volume of liquid and provided with movable tubes to convey upward the atomized mixtures.

During the period of the treatments, the portable DRAEGER analy-

## 3/

- 1) = Doses of diphenylamine equivalent to those contained in composition N. 20, with doses of oils equal to  $0.1-1 \text{ ml/m}^2$ .
- 2) = Doses of dried seaweed extracts hydrolized with alkali equivalent to those contained in composition N. 23, with doses of oils equal to  $0.1-1 \text{ ml/m}^2$ .
- 3) = Doses of animal epithelium hydrolized with acids equivalent to those contained in composition N. 24, with doses of oils equal to  $0.1-1 \text{ ml/m}^2$ .
- 4) = Doses of urea and of laurylgallate equivalent to those contained in composition N. 17, with doses of soybean oil equal to  $0.1-1 \text{ ml/m}^2$ .

Example 11

Vegetable oils as such, or concentrated non-diluted compositions based on such oils, were distributed on an Irnerium variety wheat field, using special equipment for distributing compositions with low volume of liquid (for example, 5-50 litres per hectare). Alternatively, emulsified compositions were distributed - using more conventional equipment with high volume of liquid - in 300 litres of water per hectare. Three repeated treatments were carried out at emergence, earing and blossom time, operating on large plots of 400 square meters (20x20 m) of land and leaving plots of untreated witness plants. The ozone levels detected on the field with the portable DRAEGER analyzer were, on an average, of 0.04 ppm in the morning and of 0.08 ppm in the afternoon during the period of the treatments. At harvesting time, the production in grains obtained from the differently treated plots of land was weighed. The results are reported in Table 7, which shows the considerable production increase noticed on wheat as a result of the treatments with the compositions according to the invention, even if using different distribution techniques (low or high volume of liquid).

TABLE 7

Production of Irnerium variety wheat grains at harvesting time,

zer revealed, on the poplar plantation, the presence of an average ozone level of 0.05 ppm in the morning and of 0.09 ppm in the afternoon.

The results, after 30 days from the last treatment, are reported in Table 8, from which it appears evident that the treatments with the compositions according to the invention have allowed to substantially reduce the fall of the leaves caused by the presence of high ozone levels, in respect of the untreated witness plots.

TABLE 8

Average percent of fallen leaves, in presence of harmful ozone levels, on 15 years aged Clone 314 poplar trees, 30 days after the last of two treatments carried out at intervals of 30 days with the anti-ozone compositions of the invention.

	Compositions used	Doses l/ha of oils	Average percent of fallen leaves
15	N. 4, based on refined soybean oil distributed as such	100	10.2
	N. 21, based on refined soybean oil distributed in 900 l/ha of water	100	8.5
20	N. 26, based on emulsified raw soybean oil distributed in 900 l/ha of water	100	6.0
	Untreated witness		30.5

CLAIMS

1) Composition to prevent ozone damages to cultivations, characterized in that it comprises, as an active principle, fatty acids of natural origin or their salts and esters, as in particular the triglycerides contained in oils and fats of vegetable or animal origin.

2) Composition as in claim 1), wherein the fatty acids are unsaturated fatty acids.

3) Composition as in claim 2), wherein the fatty acids are selected in the group consisting of oleic, erucic, linoleic, linolenic acids.

4) Composition as in claim 1), wherein the oils and fats of vegetable origin are selected in the group consisting of oils of linseed, soybean, sunflower, cotton, corn, safflower, grapestone, sesame, peanut, rapeseed, olive, castor-oil, tall-oil.

5) Composition as in claim 1), wherein the oils and fats of animal origin are selected in the group consisting of oils of fish, cetaceans and terrestrial Mammalia.

6) Composition as in any one of claims 1) to 5), also containing one or more compounds with antioxidant activity.

7) Composition as in claim 6), wherein the proportion of antioxidant is up to 20% by weight of the composition, and this is selected in the group consisting of alkylgallates; alkylcresols, alkylphenols and alkylanisoles; ascorbic and erythrorbic acids and their salts and esters; substituted hydroquinones; alkyldiamines; diarylamines; tocopherols; dithiopropionic acid and its salts and esters.

8) Composition as in claim 6), wherein the antioxidant is laurylgallate.

9) Composition as in claim 6), wherein the antioxidant is octylgallate.

10) Composition as in claim 6), wherein the antioxidant is dibutyl-hydroxy-toluene.

11) Composition as in claim 6), wherein the antioxidant is di-

phenylamine.

12) Composition as in claim 6), wherein the antioxidant is an alkyl ester of ascorbic acid or of its isomer erythrubic acid.

13) Composition as in any one of claims 1) to 6), also containing one or more chelating compounds for heavy metals.

14) Composition as in claim 13), wherein the proportion of chelating compound is up to 10% by weight of the composition, and this is selected in the group consisting of citric, tartaric, phosphoric acids and their salts and esters; alkylendiamino- or pentamethylen-triaminoacetates; editronic acid and its salts and esters; heptagluconates; aminoacids derived from hydrolysis of animal or vegetable proteins.

15) Composition as in any one of claims 1) to 5), also containing natural or synthetic plant growth regulators.

16) Composition as in claim 15), wherein the proportion of plant growth regulators is up to 20% by weight of the composition, and these are selected in the group consisting of dried extracts from seaweeds hydrolyzed with alkali, cytoquinines, auxines, gibberellines, and abscissic acid.

17) Composition as in any one of claims 1) to 5), also containing fertilizers.

18) Composition as in claim 17), wherein the proportion of fertilizers is up to 50% by weight of the composition, and these are selected in the group consisting of nitrogen, phosphorous, potassium synthesis compounds, oligo-elements, chelated microelements, and natural nitrogen derivatives as hydrolyzed animal or vegetable proteins.

19) Composition as in any one of claims 1) to 5), also containing surfactants and/or emulsifiers, as well as inerts.

20) Method for applying on field or tree cultivations a liquid composition as in any one of the preceding claims, characterized in that it comprises the steps of:

- possibly thinning said composition to the desired concentration, by dilution with solvents or water emulsion:

- atomizing said liquid composition as such, or else its solution or emulsion, using equipment operating on ground or air means, so as to cover the sides of the leaves having stomata;

5 - carrying out a treatment before any ozone damages are caused to the cultivations, and repeating the treatments at intervals during the vegetation period.

21) Method as in claim 20) wherein said composition is in a solid state at ambient temperature, comprising moreover the initial step of dissolving said composition into solvents.

10 22) Method as in claim 20), wherein said composition is distributed on the cultivations in an amount of between 0.1 and 100 litres per hectare of fatty acids, or of oils or fats of vegetable or animal origin.

15 23) Method as in claim 22), wherein said composition is distributed on field cultivations in an amount of between 0.1 and 50 litres per hectare of fatty acids, or of oils or fats, and preferably between 0.3 and 20 litres per hectare.

20 24) Method as in claim 22), wherein said composition is distributed on tree cultivations in an amount of between 0.2 and 100 litres per hectare of fatty acids, or of oils or fats, and preferably between 0.6 and 40 litres per hectare.

# INTERNATIONAL SEARCH REPORT

International Application No.

PCT/EP 91/00972

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (if several classification symbols apply, indicate all) <sup>6</sup>		
According to International Patent Classification (IPC) or to both National Classification and IPC Int.Cl.5                      A 01 N 37/06                      A 01 N 65/00		
<b>ii. FIELDS SEARCHED</b>		
Minimum Documentation Searched <sup>7</sup>		
Classification System	Classification Symbols	
Int.Cl.5	A 01 N	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched <sup>8</sup>		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>9</sup></b>		
Category <sup>10</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
X	US,A,3178855 (J.M. SIEGEL) 20 April 1965, see claims; column 3, lines 39-51; column 3, line 74 - column 4, line 10 ---	1-24
X	EP,A,0169663 (M.J. SAMPSON) 29 January 1986, see claims 1,2,5,7-9; page 4, line 55 ---	1-24
X	DE,A,3724595 (BTC BIOTECHNIK) 2 February 1989, see the whole document ---	1-4,15,16,19-24
X	WO,A,8303041 (BIOCHEMICAL MARKETING CORP.) 15 September 1983, see claims 1-4,6-8; page 13, lines 1-18 ---	1-4,15-24
-/-		
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p><sup>10</sup> Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&amp;" document member of the same patent family</p> </div> </div>		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search		Date of Mailing of this International Search Report
03-09-1991		26. 09. 91
International Searching Authority		Signature of Authorized Officer
EUROPEAN PATENT OFFICE		<div style="border: 1px solid black; display: inline-block; padding: 2px 10px;">M. PEIS</div> <span style="margin-left: 20px; font-family: cursive;">M. Peis</span>

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category <sup>o</sup>	Citation of Document, with indication, where appropriate, of the relevant passages	Relevant to Claim No.
X	WO,A,8910693 (SAFFER) 16 November 1989, see claims -----	1-5, 13, 14, 19- 24



**ANNEX TO THE INTERNATIONAL SEARCH REPORT  
ON INTERNATIONAL PATENT APPLICATION NO.**

EP 9100972  
SA 47577

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 20/09/91  
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A- 3178855		None	
EP-A- 0169663	29-01-86	CA-A- 1258190	08-08-89
DE-A- 3724595	02-02-89	None	
WO-A- 8303041	15-09-83	EP-A- 0103644	28-03-84
		GB-A,B 2118158	26-10-83
		JP-T- 59500319	01-03-84
		OA-A- 7578	31-03-85
WO-A- 8910693	16-11-89	AU-A- 3749489	29-11-89
		EP-A- 0413765	27-02-91
		US-A- 5030658	09-07-91